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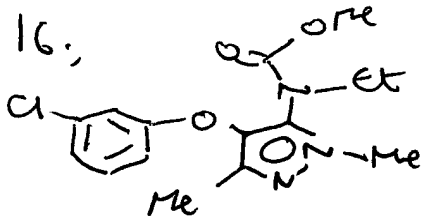

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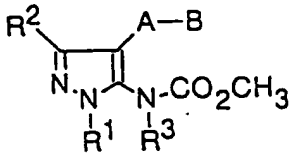
(57) An N-pyrazolyl carbamate derivative represented by the ge...



(I)

wherein R^1 and R^2 independently indicate a hydrogen atom or a C_1-C_4 alkyl group; R^3 is a hydrogen atom, a C_1-C_4 alkyl group, a C_2-C_5 alkynyl group, a C_2-C_4 alkylthioalkyl group or a C_2-C_4 alkoxyalkyl group; A is -O-, -C(O)-, $-OCH_2-$, $-CH_2O-$, $-CH_2S-$, -C≡C-, -CH=CH-, $-CH_2CH_2-$, $-CH_2ON=C(R^4)-$ or $-CH=NOC(R^4)(R^5)-$ (wher in R^4 and R^5 independently indicate a hydrog n atom or a C_1-C_4 alkyl group); and B is a hydrog n atom, an optionally substituted aryl group or an optionally substituted h terocyclic group, an agricultural/horticultural fungicide containing the N-pyrazolyl carbamate derivative as an active ingredient, and a production intermediate thereof are disclosed.

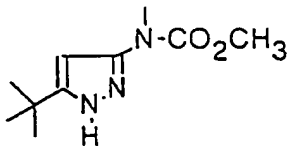
EP 0 658 547 A1

FIELD OF THE INVENTION

The present invention relates to a novel N-pyrazolyl carbamate derivative and an agricultural/horticultural fungicide containing the same as an active ingredient.

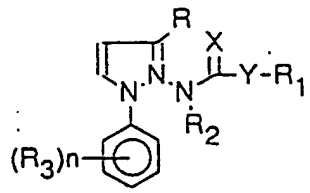
BACKGROUND OF THE INVENTION

It has hitherto been known that a certain N-pyrazolyl carbamate derivative has a biological activity such as herbicidal effect. For example, in EP129830, there is described a compound of the formula:



as a compound having a herbicidal activity.

In DE3423582, there is also described a compound of the formula:



wherein R is a cyano group or an alkoxycarbonyl group; R_1 is an alkyl group or an aryl group; R_2 is a hydrogen atom or a group of $-C(X)YR_1$; and X and Y indicate an oxygen atom or a sulfur atom, as a compound having a herbicidal activity.

However, these compounds are not necessarily suitable as an agricultural/horticultural fungicide at present.

OBJECTS OF THE INVENTION

The present inventors have intensively studied about the N-pyrazolyl carbamate derivative. As a result, it has been found that, a N-pyrazolyl carbamate derivative having a certain structure has not only excellent fungicidal activity but also extremely excellent systemicity in plants. The present invention is based on such finding.

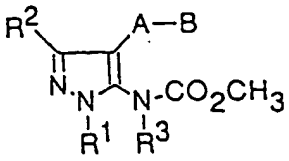
Thus, one object of the present invention is to provide a N-pyrazolyl carbamate derivative which has an excellent fungicidal activity.

Another object of the present invention is to provide an agricultural/horticultural fungicide containing the N-pyrazolyl carbamate derivative as an active ingredient, which has excellent preventive effects on various phytopathogenic fungi.

These objects as well as other objects and advantages of the present invention will become apparent to those skilled in the art from the following description.

SUMMARY OF THE INVENTION

The present invention provides a N-pyrazolyl carbamate derivative represented by the general formula (I):



(I)

wherein R^1 and R^2 independently indicate a hydrogen atom or a C_1-C_4 alkyl group; R^3 is a hydrogen atom, a C_1-C_4 alkyl group, a C_2-C_5 alkynyl group, a C_2-C_4 alkylthioalkyl group or a C_2-C_4 alkoxyalkyl group; A is -O-, -C(O)-, $-OCH_2-$, $-CH_2O-$, $-CH_2S-$, -C≡C-, -CH=CH-, $-CH_2CH_2-$, $-CH_2ON=C(R^4)-$ or $-CH=NOC(R^4)(R^5)-$ (wherein R^4 and R^5 independently indicate a hydrogen atom or a C_1-C_4 alkyl group); and B is a hydrogen atom, an optionally substituted aryl group or an optionally substituted heterocyclic group.

The present invention also provides an agricultural/horticultural fungicide containing the same as an active ingredient.

DETAILED DESCRIPTION OF THE INVENTION

The present invention will be explained in detail below.

The N-pyrazolyl carbamate derivative of the present invention is represented by the above formula (I). In the above formula (I), R^1 and R^2 independently indicate a hydrogen atom; or a C_1-C_4 alkyl group such as methyl group, ethyl group, n-propyl group, iso-propyl group, n-butyl group, sec-butyl group, etc. They indicate preferably hydrogen atom, methyl group or ethyl group, and more preferably, methyl group.

R^3 is a hydrogen atom; a C_1-C_4 alkyl group such as methyl group, ethyl group, n-propyl group, iso-propyl group, n-butyl group, sec-butyl group, etc.;a C_2-C_5 alkynyl group such as ethynyl group, propargyl group, butynyl group, pentynyl group, etc.; a C_2-C_4 alkylthioalkyl group such as methylthiomethyl group, ethylthiomethyl group, etc.; or a C_2-C_4 alkoxyalkyl group such as methoxymethyl group, ethoxymethyl group, methoxyethyl group, ethoxyethyl group, etc. It is preferably hydrogen atom, C_2-C_5 alkynylgroup or C_2-C_4 alkoxyalkyl group.

A is -O-, -C(O)-, $-OCH_2-$, $-CH_2O-$, $-CH_2S-$, -C≡C-, -CH=CH-, $-CH_2CH_2-$, $-CH_2ON=C(R^4)-$ or $-CH=NOC(R^4)(R^5)-$. It is preferably -O-, $-OCH_2-$, $-CH_2O-$, $-CH_2S-$, -C≡C-, -CH=CH-, $-CH_2ON=C(R^4)-$ or $-CH=NOC(R^4)(R^5)-$, and more preferably, $-OCH_2-$, $-CH_2O-$, $-CH_2S-$, -C≡C-, $-CH_2ON=C(R^4)-$ or $-CH=NOC(R^4)(R^5)-$. R^4 and R^5 independently indicate a hydrogen atom; or a C_1-C_4 alkyl group such as methyl group, ethyl group, n-propyl group, iso-propyl group, n-butyl group, sec-butyl group, etc. They indicate preferably hydrogen atom or C_1-C_2 alkyl group. More preferably, R^4 is a hydrogen or a methyl group and R^5 is a hydrogen atom.

B is a hydrogen atom; an optionally substituted aryl group such as phenyl group, naphthyl group, etc.; or an optionally substituted heterocyclic group such as pyridyl group, pirimidyl group, furanyl group, benzothiazolyl group, etc. It is preferably optionally substituted phenyl group , naphthyl group or pyridyl group, and more preferably, optionally substituted phenyl group.

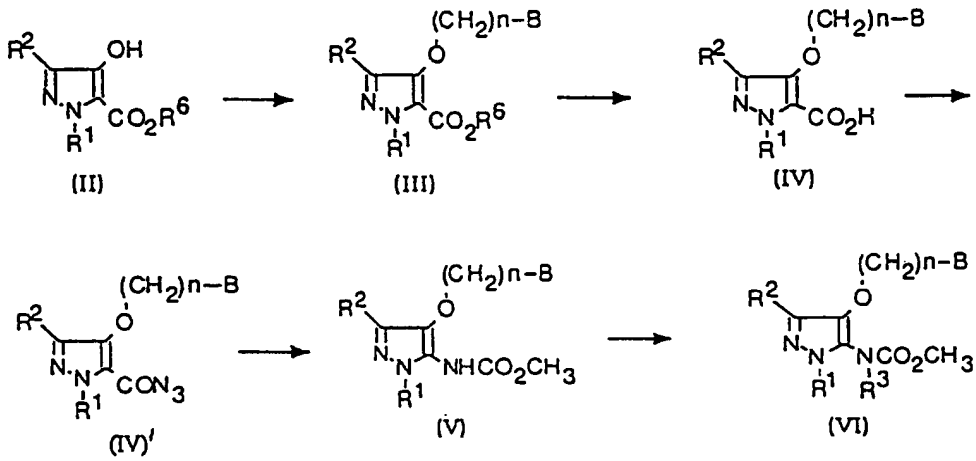
The aryl group and heterocyclic group may be substituted with a substituent selected from a group consisting of the following substituents: a cyano group; a nitro group; a halogen atom such as fluorine atom, chlorine atom, bromine atom, etc.; a C_1-C_4 alkyl group such as methyl group, ethyl group, n-propyl group, iso-propyl group, n-butyl group, sec-butyl group, etc.; a C_1-C_4 haloalkyl group such as trifluoromethyl group, difluoromethyl group, trichloromethyl group, dichlorodifluoroethyl group etc.; a C_1-C_6 alkoxy group such as methoxy group, ethoxy group, iso-propoxy group, n-butoxy group, etc. which may be substituted with a halogen atom or a C_3-C_6 cycloalkyl group; a C_1-C_6 alkylthio group such as methylthio group, ethylthio group, iso-propylthio group, n-butylthio group, etc.; a C_2-C_6 alkenyloxy group such as propenyloxy group, etc. which may be substituted with a halogen atom; a C_2-C_6 alkynyloxy group such as propargyloxy group, etc.; and a phenoxy group, a benzyloxy group, or a pyridyloxy group which may be substituted by the just mentioned cyano group, nitro group, halogen atom, C_1-C_4 alkyl group, C_1-C_4 haloalkyl group, C_1-C_6 alkoxy group, C_1-C_6 alkylthio group, C_1-C_6 alkenyloxy group, or C_1-C_6 alkynyloxy group.

Further, adjacent two substituents may bond together with an aryl group or a h terocyclic group to form a fused ring. Th number of the substituent is 0 to 5, preferably 0 to 3. When containing a plurality of substituents, the substituents may be th same or different. Preferable examples of the substituent include halogen atom, C_1-C_4 alkyl group, C_1-C_4 haloalkyl group, C_1-C_6 alkoxy group which may be substituted with a halogen atom, phenoxy group and the like. More pref rable examples of the substituent include halogen

atom; C_1-C_4 alkyl group; C_1-C_4 alkoxy group which may be substituted with a halogen atom, preferably with a fluorine atom; trifluoromethyl group; phenoxy group and the like.

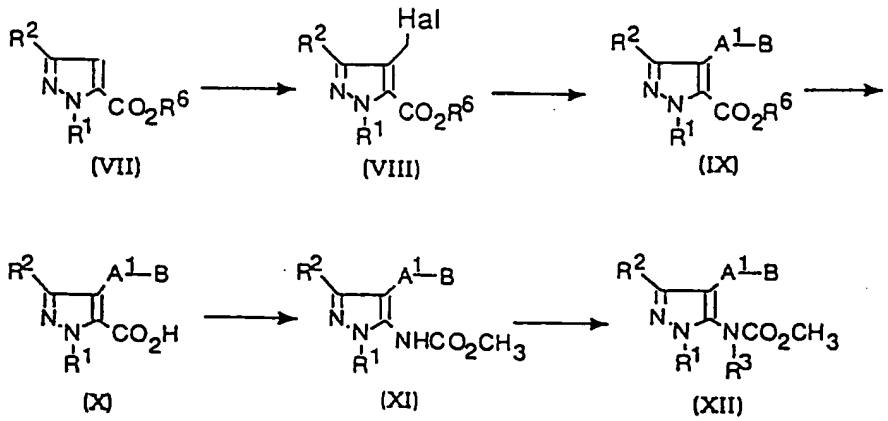
All compounds of the present invention are novel and they can be produced according to the following reaction scheme 1, 2 or 3.

(Reaction scheme 1)

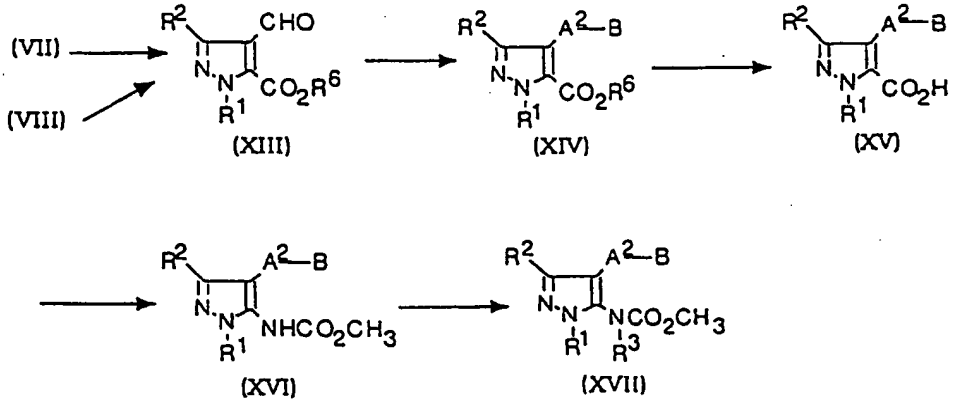


In the above reaction scheme, R^1, R^2, R^3 and B are as defined in the above general formula (I); R^6 is a C_1-C_4 alkyl group; and n is 0 or 1.

(Reaction scheme 2)



(Reaction scheme 3)



In the reaction schemes 2 and 3, R^1, R^2, R^3 and B are as defined in the above general formula (I); Hal is a chlorine atom or a bromine atom; R^6 is a C_1-C_4 alkyl group; A^1 is $-CH_2O-$, $-CH_2S-$ or $-CH_2ON=C(R^4)-$ and A^2 is $-CH=NOC(R^4)(R^5)-$.

The above reaction scheme 1 shows a method comprising reacting a 4-hydroxy-5-alkoxycarbonyl pyrazole derivative (II) with a halide $-(CH_2)_nB$ in the presence of a base to give a corresponding ether derivative (III); converting a carboxylic acid derivative (IV), obtained by hydrolyzing an ester group with a suitable base, into a carboxylic acid halide with a halogenating agent; and then subjecting an azide derivative (IV)', obtained by treating sodium azide, to the Curtius rearrangement reaction in methanol to give a carbamate derivative (V). The carbamate derivative (V) can be reacted with a corresponding halide in the presence of a base to give a compound (IV). Further, 4-hydroxy-5-alkoxycarbonyl pyrazole (II) as a starting material can be produced by a method described in Japanese Patent Application No. 4-217668 or a similar method.

Examples of the base used in the reaction from (II) to (III) and the reaction from (V) to (VI) include alkali metal hydrides such as sodium hydride, etc.; alkali metal alcolat s such as sodium methylate, etc.; alkali metal carbonates such as potassium carbonate, etc.; alkali metal hydroxides such as potassium hydroxide, tc. Preferabl xamples include alkali metal hydrides and alkali m tal carbonates.

Examples of th base used in the reaction from (III) to (IV) include alkali metal hydroxid s such as sodium hydroxide, potassium hydroxide, etc.

Examples of the halogenating agent used in the reaction from (IV) to carboxylic acid halide include thionyl chloride, phosgene or phosphorous oxychloride. In this reaction, there can be used tertiary amines such as N-methylmorpholine, triethylamine, etc., aromatic bases such as pyridine, picoline, etc. in an inert solvent. The following solvent may be used alone in the azidation reaction, or the reaction may be carried out in two kinds of solvents in the presence or absence of a normal phase transfer catalyst.

Examples of the solvent used in these reactions include water; alcohols such as methanol, ethanol, etc.; ethers such as diethyl ether, tetrahydrofuran, etc.; polar solvents such as dimethylformamide, dimethyl sulfoxide, etc.; aromatic hydrocarbons such as toluene, chlorobenzene, etc.; alkyl halides such as methylene chloride, dichloroethane, etc.

The reaction scheme 2 shows a method comprising subjecting a 5-alkoxycarbonyl pyrazole derivative (VII) to chloromethylation or bromomethylation, converting into an ether, thioether or iminooxy derivative (IX) and then preparing carbamate derivatives (XI) and (XII) according to the same manned as that described in the reaction scheme 1.

The chloromethylation or bromomethylation reaction from (VII) to (VIII) can be carried out according to a method described in Org. Synth., III, 195 or a similar method. The derivative (VIII) can be reacted with B-OH, B-SH or an oxime derivative in an inert solvent {e.g., alcohols such as methanol, ethanol, etc.; ethers such as diethyl ether, tetrahydrofuran, etc.; polar solvents such as dimethylformamide (DMF), dimethyl sulfoxide, etc.; aromatic hydrocarbons such as toluene, chlorobenzene, etc.} in the presence of a suitable base (e.g., alkali metal hydrides such as sodium hydride, etc.; alkali metal alcoholates such as sodium methylate, etc.; alkali metal carbonates such as potassium carbonate, etc.; alkali metal hydroxides such as potassium hydroxide, etc.) to give an ether, thioether or iminooxy derivative (IX).

The reaction scheme 3 shows a method comprising subjecting a 5-alkoxycarbonyl pyrazole derivative (VII) to the Vilsmeirer reaction or subjecting a chloromethyl or bromomethyl derivative (VIII) to the oxidation reaction to give an aldehyde derivative (XIII) and, after subjecting to imination, preparing carbamate derivatives (XVI) and (XVII).

The Vilsmeirer reaction of the compound (VII) itself is a known method and can be carried out according to a method described in Org. Synth., III, 98 (1955) or Zh. Org. Khim., 9, 815 (1973) or a similar method. The oxidation reaction of the compound (VIII) can be carried out by a method of treating N-oxide of tertiary amine (e.g., N-methylmorpholine or triethylamine) in an inert solvent (e.g., methylene chloride or acetonitrile).

The resulting aldehyde derivative (XIII) can be reacted with a corresponding oxyamine derivative in an inert solvent (e.g., alcohols such as methanol, ethanol, etc.; ethers such as diethyl ether, tetrahydrofuran, etc.; polar solvents such as dimethylformamide, dimethyl sulfoxide, etc.; aromatic hydrocarbons such as toluene, chlorobenzene, etc.) to give an imino derivative (XIV).

All reactions described in reaction schemes 1 to 3 are carried out at a temperature within a range from -20 °C to the boiling point of the solvent to be used.

The compounds of the present invention thus obtained are each novel one having an excellent fungicidal activity. They exert excellent preventive effects on various phytopathogenic fungi, which makes them useful as an agricultural/ horticultural fungicide.

For example, the compound of the present invention has a high activity against rice blast (Pyricularia oryzae), rice sheath blight (Rhizoctonia solani), wheats powdery mildow (Erysiphe graminis f. sp. tritici), barley powdery mildow (E. graminis f. sp. hodei), various leaf rusts of wheat and barley (e.g., Puccinia recondita), gray mold of vegetables and fruit trees (Botrytis cinerea), late blight of various crops (Phytophthora infestance) and the like. Further, they have prolonged residual activity and excellent systemicity in plants, which makes them highly useful as an agricultural/horticultural fungicide.

When using the compound of the present invention as an agricultural/horticultural fungicide, the compound may be used as it is. It is preferable to formulate said compound into, for example, emulsifiable concentrates, wettable powders, dust or granules by blending with adjuvants in a conventional manner to thereby ensure the effective dispersion of the active ingredient at the application.

When using the agricultural/horticultural fungicide of the present invention in the form of emulsifiable concentrate, a raw material obtained by mixing 10 to 80 parts (preferably 10 to 70 parts) of the compound of th pr sent invention, 10 to 90 parts (preferably 20 to 80 parts) of a solv nt and 3 to 20 parts (preferably 5 to 15 parts) of a surfactant is diluted with water to a predetermined concentration and the r sulting chemical solution is applied by a method such as spraying.

When using the fungicid in the form of wettable powder, a raw material obtained by mixing 5 to 80 parts (preferably 10 to 70 parts) of the compound of the present invention, 10 to 90 parts (preferably 20 to

80 parts) of an xtender and 1 to 20 parts (preferably 3 to 15 parts) of a surfactant is diluted with water to a predetermined concentration according to the same manner as the case of emulsifiable concentrate.

When using the fungicide in the form of dust, a raw material obtained by mixing 0.1 to 10 parts (preferably 1 to 5 parts) of the compound of the present invention and 90 to 99.9 parts (preferably 95 to 99 parts) of an extender such as kaolin, bentonite, talc , etc. is used as it is.

The agricultural/horticultural fungicide of the present invention can also be used after mixing with other active ingredients which do not inhibit the fungicidal effect of the active ingredient of the present invention such as fungicides, insecticides, acarcides and the like.

The agricultural/horticultural fungicide of the present invention can be suitably applied for both foliar application and submerged application. In case of foliar application, emulsifiable concentrates or wettable powders are normally diluted with water to the concentration (concentration of active ingredient) of 10 to 1000 ppm and the resulting solution may be applied in an amount of 10 to 500 liters per 10 ares.

Among the compounds represented by the above formulas (VIII) and (XIII), a compound wherein R^1 and R^2 indicate an C_1-C_4 alkyl group is novel and is useful as a production intermediate of the compound of the general formula (I).

As described above, all compounds of the present invention are novel compounds and they have an excellent fungicidal activity. Since the compound of the present invention has an excellent control effect on various phytopathogenic fungi, it is useful as an agricultural/horticultural fungicide.

Examples

The following Examples further illustrate the present invention in detail but are not to be construed as to limiting the scope thereof.

Example 1

Synthesis of methyl N-{1,3-dimethyl-4-(2,5-dimethylbenzyloxy)pyrazole-5-yl}-N-propargyl-carbamate (compound No. 50 in Table 1)

A DMF solution (10 ml) of methyl 1,3-dimethyl-4-hydroxypyrazole-5-ylcarboxylate (1 g), 2,5-dimethylbenzyl chloride (0.95 g) and K_2CO_3 (0.98 g) were heated with stirring for 2 hours. 30 ml of ethyl acetate was added, and the mixture was washed in turn with water and brine and then dried over anhydrous sodium sulfate. The solvent was distilled off to give a crude benzyl ether derivative (1.5 g).

An aqueous NaOH solution (NaOH: 0.25 g, H_2O: 5 ml) was added to an ethanol (5 ml) solution of the benzyl ether derivative (1.5 g) and the mixture was heated under reflux condition for two hours. After cooling, it was neutralized by adding concentrated HCl (0.65 ml), followed by extracting with 30 ml of ethyl acetate. Then, the organic layer was washed in turn with water and brine and dried over anhydrous sodium sulfate. The solvent was distilled off and the resulting residue was recrystallized from a mixed solvent of ethyl acetate/hexane to give a carboxylic acid derivative (1.4 g).

To 15 ml of a methylene chloride solution of the carboxylic acid derivative (1.4 g), pyridine (0.7 g) and thionyl chloride (0.77 g) were added in turn under water cooling. After stirring for 2 hours, an aqueous sodium aside solution (NaN_3: 0.5 g, H_2O: 2 ml) and $(n\text{-}C_4H_9)_4NCl$ (0.05 g) were added. After stirring for 3 hours, 30 ml of methylene chloride was added, and the organic layer was washed in turn with water and brine and then dried over anhydrous sodium sulfate. The solvent was distilled off to give a crude azide derivative (1.5 g).

To the crude aside derivative (1.5 g), 20 ml of methanol was added and the mixture was heated under reflux condition for 4 hours. After the solvent was distilled off, the residue was chromatographed (SiO_2: 50 g, hexane/ethyl acetate = 1/1) to give a 1.3 g of methyl N-{1,3-dimethyl-4-(2,5-dimethylbenzyloxy)pyrazole-5-yl} carbamate (compound No. 48 in Table 1).

To 5 ml of a DMF solution of the carbamate derivative (0.8 g, compound No. 48 in Table 1), 60% NaH (0.11 g) was added and the mixture was stirred for 20 minutes. Then, propargyl bromide (1 g) was added, followed by stirring for one hour. After 30 ml of ethyl acetate was added, the mixture was washed in turn with water and brine and dried over anhydrous sodium sulfate. The solvent was distilled off, and then the residue was chromatographed (SiO_2: 50 g, hexane/ethyl acetate = 1/1) to give 0.8 g of a titled compound.

Example 2

Synthesis of methyl N-[1,3-dimethyl-4-{(α-methyl-4-trifluoromethyl-benzylidene)aminooxymethyl pyrazole-5-yl}]-N-propargyl-carbamate (compound No. 169 in Table 1)

To a solution of ethyl 1,3-dimethylpyrazole-5-ylcarboxylate (16.3 g), phosphoric acid (11 ml), concentrated hydrochloric (27 ml) and acetic acid (50 ml), paraformaldehyde (6 g) was added and the mixture was heated at 100 °C with stirring for 5 hours. After cooling, the reaction mixture was poured into ice and neutralized with Na_2CO_3, and extracted with 200 ml of ethyl acetate. The extract was washed in turn with water and brine and dried over anhydrous sodium sulfate. The solvent was distilled off and the residue was chromatographed (SiO_2: 150 g, hexane/ethyl acetate = 4/1) to give 8 g of ethyl 4-chloromethyl-1,3-dimethylpyrazole-5-ylcarboxylate.

^{1}H-NMR ($CDCl_3$); 1.42 (3H, t), 2.30 (3H, s), 4.12 (3H, s), 4.42 (2H, q), 4.75 (2H, s)

60% NaH (0.2 g) was added to a DMF solution (5 ml) of 4-trifluoromethylacetophenone oxime (1 g) and the mixture was stirred for 20 minutes. Then, ethyl 4-chloromethyl-1,3-dimethylpyrazole-5-ylcarboxylate (1 g) was added and the mixture was stirred and allowed to stand overnight. After 30 ml of ethyl acetate was added, the organic layer was washed in turn with water and brine and then dried over anhydrous sodium sulfate. The solvent was distilled off to give a crude oxime ether derivative (1.8 g).

To 10 ml of an ethanol solution of the oxime ether derivative (1.8 g), an aqueous NaOH solution (NaOH: 0.24 g, H_2O: 5 ml) was added and the mixture was heated under reflux condition for 2 hours. After cooling, the reaction mixture was neutralized by adding concentrated HCl (0.6 ml). After 30 ml of ethyl acetate was added, the organic layer was washed in turn with water and saturated saline and then dried over anhydrous sodium sulfate. The solvent was distilled off and the resulting residue was recrystallized from a mixed solvent of ethyl acetate/hexane to give a carboxylic acid derivative (1.6 g).

To 15 ml of a methylene chloride solution of the carboxylic acid derivative (1.6 g), pyridine (0.6 g) and thionyl chloride (0.6 g) were added in turn under water cooling. After stirring for 2 hours, an aqueous sodium azide solution (NaN_3: 0.4 g, H_2O: 2 ml) and $(n\text{-}C_4H_9)_4NCl$ (0.05 g) were added. After stirring for 3 hours, 30 ml of methylene chloride was added, and the organic layer was washed in turn with water and brine and then dried over anhydrous sodium sulfate. The solvent was distilled off to give a crude azide derivative (1.6 g).

To the crude azide derivative (1.6 g), 20 ml of methanol was added and the mixture was heated under reflux condition for 4 hours. After the solvent was distilled off, the residue was chromatographed (SiO_2: 50 g, hexane/ethyl acetate = 1/1) to give a 1.4 g of methyl N-[1,3-dimethyl-4-{(α-methyl-4-trifluoromethylbenzylidene)aminooxymethyl pyrazole-5-yl}] carbamate (compound No. 167 in Table 1).

To 5 ml of a DMF solution of the carbamate derivative (1.4 g, compound No. 167 in Table 1), 60% NaH (0.16 g) was added and the mixture was stirred for 20 minutes. Then, propargyl bromide (1 g) was added and the mixture was stirred for one hour. After 30 ml of ethyl acetate was added, the mixture was washed in turn with water and brine and then dried over anhydrous sodium sulfate. After the solvent was distilled off, the residue was chromatographed (SiO_2: 50 g, hexane/ethyl acetate = 1/1) to give 1.2 g of a titled compound.

Example 3

Synthesis of N-{1,3-dimethyl-4-(α-methyl-3-trifluoromethyl-benzyloxyiminomethyl)pyrazole-5-yl} carbamate (compound No. 194 in Table 1)

To a mixture of ethyl 1,3-dimethylpyrazole-5-ylcarboxylate (20.0 g) and a 30% hydrogen bromide-acetic acid solution (60 ml), paraformaldehyde (7.2 g) was added and the mixture was stirred at 80 - 90 °C for 2 hours and a half. The reaction mixture was poured into ice water and the solution was neutralized with sodium acetate trihydrate (41 g). After extracting with ethyl acetate, the extract was washed in turn with an aqueous saturated sodium bicarbonate solution and brine and then dried over anhydrous sodium sulfate. After the solvent was distilled off, the residue was chromatographed (SiO_2: 200 g, hexane/ethyl acetate = 4/1) to give 26.8 g of ethyl 4-bromomethyl-1,3-dimethylpyrazole-5-ylcarboxylate (yield: 86.3%).

^{1}H-NMR ($CDCl_3$); 1.45 (3H, t), 2.28 (3H, s), 4.09 (3H, s), 4.42 (2H, q), 4.65 (2H, s),

^{13}C-NMR ($CDCl_3$); 11.3, 14.1, 23.2, 39.8, 61.4, 120.3, 130.3, 147.1, 159.7

To 20 ml of an acetonitrile solution of ethyl 4-bromomethyl-1,3-dim thylpyrazole-5-ylcarboxylate (2.9 g, 11.1 mmol) and molecular sieves 4A (3 g), N-methylmorpholine-N-oxid (2.6 g, 22.2 mmol) was added under water cooling, followed by stirring at room temperature for 48 hours. Th mixed solution was filtered

with celite and the filtrate was concentrated. To the resulting residue, ethyl ac tat was added and th mixture was washed in turn with water and brine and then dried over anhydrous sodium sulfate. After the solvent was distilled off, the resulting residue was recrystallized from hexane/ethyl acetate to give 1.7 g of ethyl 1,3-dimethyl-4-formylpyrazole-5-ylcarboxylate (yield: 78%).

^{1}H-NMR ($CDCl_3$); 1.44 (3H, t), 2.49 (3H, s), 4.14 (3H, s), 4.47 (2H, q), 10.39 (1H, s)

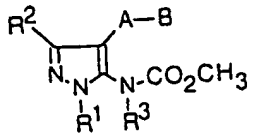
To 15 ml of an ethanol solution of ethyl 1,3-dimethyl-4-formylpyrazole-5-ylcarboxylate (1.5 g, 7.65 mmol), α-methyl-3-trifluoromethylbenzyloxyamine (1.6 g, 7.80 mmol) was added and the mixture was stirred at room temperature for 12 hours. The reaction solution was concentrated and the residue was chromatographed (SiO_2: 40 g, hexane/ethyl acetate = 4/1) to give 2.5 g of ethyl {1,3-dimethyl-4-(α-methyl-3-trifluoromethyl-benzyloxyiminomethyl)pyrazole-5-yl} carboxylate (yield: 85.3%).

^{1}H-NMR ($CDCl_3$); 1.42 (3H, t), 1.63 (3H, d), 2.23 (3H, s), 4.07 (3H, s), 4.40 (2H, q), 4.73 (1H, q), 7.4-7.65 (4H, m), 8.56 (1H, s)

According to the same manner as that described in Examples 1 and 2, the resulting ethyl carboxylate derivative (2.5 g) was subjected in turn to hydrolysis, azidation and Curtius rearrangement reactions to give the titled compound (1.9 g).

According to the same manner as that described above except for an alteration in the starting material, a compound in Table 1 can be synthesized.

Table 1



Compound No.	R1	R2	R3	A	B	Physical properties
1	CH3	CH3	H	O	H	White crystal
2	CH3	CH3	H	O	5-CF3-pyridin-2-yl	White crystal
3	CH3	CH3	CH2OCH3	O	5-CF3-pyridin-2-yl	Viscous liquid
4	CH3	CH3	propargyl	O	5-CF3-pyridin-2-yl	Viscous liquid
5	CH3	CH3	CH2SCH3	O	5-CF3-pyridin-2-yl	Viscous liquid
6	CH3	CH3	CH2OCH3	O	4-CF3-pyridin-2-yl	Viscous liquid
7.	CH3	CH3	propargyl	O	4-CF3-pyridin-2-yl	Viscous liquid
8	CH3	CH3	CH2OCH3	O	3-CF3-pyridin-2-yl	Viscous liquid
9	CH3	CH3	propargyl	O	3-CF3-pyridin-2-yl	Viscous liquid
10	CH3	CH3	CH2OCH3	O	4-CF3-6-Cl-pyridin-2-yl	Viscous liquid
11	CH3	CH3	propargyl	O	4-CF3-6-Cl-pyridin-2-yl	Viscous liquid
12	CH3	CH3	CH2OCH3	O	4-Cl-pyridin-2-yl	Viscous liquid
13	CH3	CH3	C2H5	O	4-Cl-pyridin-2-yl	Viscous liquid
14	CH3	CH3	propargyl	O	4,6-Cl2-pyridin-2-yl	Viscous liquid
15	CH3	CH3	propargyl	O	5-Cl-2-NO2-phenyl	Viscous liquid
16	CH3	CH3	C2H5	O	3-Cl-phenyl	Viscous liquid
17	CH3	CH3	propargyl	O	3-PhO-phenyl	Viscous liquid
18	CH3	CH3	propargyl	O	3-Cl-4-NO2-phenyl	Viscous liquid
19	CH3	CH3	propargyl	O	6-(2'-CN-PhO)pyrimidin-4-yl	Viscous liquid
20	CH3	CH3	propargyl	O	4-(2'-CN-PhO)pyrimidin-2-yl	Viscous liquid
21	CH3	CH3	H	OCH2	Phenyl	White crystal
22	CH3	CH3	CH2OCH3	OCH2	Phenyl	Viscous liquid
23	CH3	CH3	propargyl	OCH2	Phenyl	Viscous liquid
24	CH3	CH3	CH2SCH3	OCH2	Phenyl	Viscous liquid
25	CH3	CH3	H	OCH2	3-Cl-phenyl	White crystal

Table 1 (Continued)

	R1	R2	R3	A	B	
26	CH3	CH3	C2H5	OCH2	3-Cl-phenyl	Viscous liquid
27	CH3	CH3	CH2OCH3	OCH2	3-Cl-phenyl	Viscous liquid
28	CH3	CH3	CH2SCH3	OCH2	3-Cl-phenyl	Viscous liquid
29	CH3	CH3	propargyl	OCH2	3-Cl-phenyl	Viscous liquid
30	CH3	CH3	propargyl	OCH2	2-Cl-phenyl	Viscous liquid
31	CH3	CH3	CH2OCH3	OCH2	2-Cl-phenyl	Viscous liquid
32	CH3	CH3	propargyl	OCH2	4-Cl-phenyl	Viscous liquid
33	CH3	CH3	CH2OCH3	OCH2	4-Cl-phenyl	Viscous liquid
34	CH3	CH3	propargyl	OCH2	2,4-Cl2-phenyl	Viscous liquid
35	CH3	CH3	CH2OCH3	OCH2	2,4-Cl2-phenyl	Viscous liquid
36	CH3	CH3	H	OCH2	2,5-Cl2-phenyl	White crystal
37	CH3	CH3	C2H5	OCH2	2,5-Cl2-phenyl	Viscous liquid
38	CH3	CH3	CH2OCH3	OCH2	2,5-Cl2-phenyl	Viscous liquid
39	CH3	CH3	CH2SCH3	OCH2	2,5-Cl2-phenyl	Viscous liquid
40	CH3	CH3	propargyl	OCH2	2,5-Cl2-phenyl	Viscous liquid
41	CH3	CH3	CH2OCH3	OCH2	2-Me-phenyl	Viscous liquid
42	CH3	CH3	propargyl	OCH2	2-Me-phenyl	Viscous liquid
43	CH3	CH3	CH2OCH3	OCH2	3-Me-phenyl	Viscous liquid
44	CH3	CH3	propargyl	OCH2	3-Me-phenyl	Viscous liquid
45	CH3	CH3	propargyl	OCH2	4-Me-phenyl	Viscous liquid
46	CH3	CH3	propargyl	OCH2	2,4-Me2-phenyl	Viscous liquid
47	CH3	CH3	CH2OCH3	OCH2	2,4-Me2-phenyl	Viscous liquid
48	CH3	CH3	H	OCH2	2,5-Me2-phenyl	White crystal
49	CH3	CH3	CH2OCH3	OCH2	2,5-Me2-phenyl	Viscous liquid
50	CH3	CH3	propargyl	OCH2	2,5-Me2-phenyl	Viscous liquid
51	CH3	CH3	CH2OCH3	OCH2	2-Me-5-Cl-phenyl	Viscous liquid
52	CH3	CH3	propargyl	OCH2	2-Me-5-Cl-phenyl	Viscous liquid
53	CH3	CH3	CH2OCH3	OCH2	2-Me-5-SMe-phenyl	Viscous liquid
54	CH3	CH3	propargyl	OCH2	2-CHF2O-phenyl	Viscous liquid
55	CH3	CH3	CH2OCH3	OCH2	2-CHF2O-phenyl	Viscous liquid

Table 1 (Continued)

56	CH3	CH3	propargyl	OCH2	3-CHF2O-phenyl	Viscous liquid
57	CH3	CH3	CH2OCH3	OCH2	3-CHF2O-phenyl	Viscous liquid
58	CH3	CH3	propargyl	OCH2	4-CHF2O-phenyl	Viscous liquid
59	CH3	CH3	CH2OCH3	OCH2	4-CHF2O-phenyl	Viscous liquid
60	CH3	CH3	propargyl	OCH2	2-Me-4-CHF2O-phenyl	Viscous liquid
61	CH3	CH3	CH2OCH3	OCH2	2-Me-5-CHF2O-phenyl	Viscous liquid
62	CH3	CH3	H	OCH2	2-Cl-4-CHF2O-phenyl	White crystal
63	CH3	CH3	CH2OCH3	OCH2	2-Cl-4-CHF2O-phenyl	Viscous liquid
64	CH3	CH3	propargyl	OCH2	2-Cl-4-CHF2O-phenyl	Viscous liquid
65	CH3	CH3	H	OCH2	2-Cl-5-CHF2O-phenyl	Viscous liquid
66	CH3	CH3	CH2OCH3	OCH2	2-Cl-5-CHF2O-phenyl	Viscous liquid
67	CH3	CH3	propargyl	OCH2	2-Cl-5-CHF2O-phenyl	Viscous liquid
68	CH3	CH3	H	OCH2	5-Cl-2-CHF2O-phenyl	Viscous
69	CH3	CH3	CH2OCH3	OCH2	5-Cl-2-CHF2O-phenyl	Viscous liquid
70	CH3	CH3	propargyl	OCH2	5-Cl-2-CHF2O-phenyl	Viscous liquid
71	CH3	CH3	H	OCH2	2,5-(CHF2O)2-phenyl	White crystal
72	CH3	CH3	CH2OCH3	OCH2	2,5-(CHF2O)2-phenyl	Viscous liquid
73	CH3	CH3	propargyl	OCH2	2,5-(CHF2O)2-phenyl	Viscous liquid
74	CH3	CH3	propargyl	OCH2	2,4-(CHF2O)2-phenyl	Viscous liquid
75	CH3	CH3	C2H5	OCH2	3-PhO-phenyl	Viscous liquid
76	CH3	CH3	CH2OCH3	OCH2	3-PhO-phenyl	Viscous liquid
77	CH3	CH3	propargyl	OCH2	3-PhO-phenyl	Viscous liquid
78	CH3	CH3	propargyl	OCH2	2-CF3-phenyl	Viscous liquid
79	CH3	CH3	propargyl	OCH2	3-CF3-phenyl	Viscous liquid
80	CH3	CH3	propargyl	OCH2	4-CF3-phenyl	Viscous liquid
81	CH3	CH3	CH2OCH3	OCH2	2,5-(CF3)2-phenyl	Viscous liquid
82	CH3	CH3	propargyl	OCH2	2,5-(CF3)2-phenyl	Viscous liquid
83	CH3	CH3	CH2OCH3	OCH2	3,5-(CF3)2-phenyl	Viscous liquid
84	CH3	CH3	propargyl	OCH2	3,5-(CF3)2-phenyl	Viscous liquid
85	CH3	CH3	propargyl	OCH2	3-benzyloxy-phenyl	Viscous liquid

Table 1 (Continued)

86	CH3	CH3	propargyl	OCH2	2-naphthyl	Viscous liquid
87	CH3	CH3	CH2OCH3	OCH2	2-naphthyl	Viscous liquid
88	CH3	CH3	propargyl	OCH2	3-naphthyl	Viscous liquid
89	CH3	CH3	CH2OCH3	OCH2	3-naphthyl	Viscous liquid
90	CH3	CH3	propargyl	OCH2	2,2-Me2-dihydrobenzofuran-5-yl	Viscous liquid
91	CH3	CH3	H	CH2O	Phenyl	White crystal
92	CH3	CH3	CH2OCH3	CH2O	Phenyl	Viscous liquid
93	CH3	CH3	propargyl	CH2O	Phenyl	Viscous liquid
94	CH3	CH3	CH2SCH3	CH2O	Phenyl	Viscous liquid
95	CH3	CH3	H	CH2O	3-Cl-phenyl	White crystal
96	CH3	CH3	C2H5	CH2O	3-Cl-phenyl	Viscous liquid
97	CH3	CH3	CH2OCH3	CH2O	3-Cl-phenyl	Viscous liquid
98	CH3	CH3	CH2SCH3	CH2O	3-Cl-phenyl	Viscous liquid
99	CH3	CH3	propargyl	CH2O	3-Cl-phenyl	Viscous liquid
100	CH3	CH3	propargyl	CH2O	2-Cl-phenyl	Viscous liquid
101	CH3	CH3	CH2OCH3	CH2O	2-Cl-phenyl	Viscous liquid
102	CH3	CH3	propargyl	CH2O	4-Cl-phenyl	Viscous liquid
103	CH3	CH3	CH2OCH3	CH2O	4-Cl-phenyl	Viscous liquid
104	CH3	CH3	propargyl	CH2O	2,4-Cl2-phenyl	Viscous liquid
105	CH3	CH3	CH2OCH3	CH2O	2,4-Cl2-phenyl	Viscous liquid
106	CH3	CH3	H	CH2O	2,5-Cl2-phenyl	White crystal
107	CH3	CH3	C2H5	CH2O	2,5-Cl2-phenyl	Viscous liquid
108	CH3	CH3	CH2OCH3	CH2O	2,5-Cl2-phenyl	Viscous liquid
109	CH3	CH3	CH2SCH3	CH2O	2,5-Cl2-phenyl	Viscous liquid
110	CH3	CH3	propargyl	CH2O	2,5-Cl2-phenyl	Viscous liquid
111	CH3	CH3	CH2OCH3	CH2O	2-Me-phenyl	Viscous liquid
112	CH3	CH3	propargyl	CH2O	2-Me-phenyl	Viscous liquid
113	CH3	CH3	CH2OCH3	CH2O	3-Me-phenyl	Viscous liquid
114	CH3	CH3	propargyl	CH2O	3-Me-phenyl	Viscous liquid
115	CH3	CH3	propargyl	CH2O	4-Me-phenyl	Viscous liquid

Table 1 (Continued)

116	CH3	CH3	H	CH2O	2,4-Me2-phenyl	Viscous liquid
117	CH3	CH3	propargyl	CH2O	2,4-Me2-phenyl	Viscous liquid
118	CH3	CH3	H	CH2O	2,5-Me2-phenyl	White crystal
119	CH3	CH3	CH2OCH3	CH2O	2,5-Me2-phenyl	Viscous liquid
120	CH3	CH3	propargyl	CH2O	2,5-Me2-phenyl	Viscous liquid
121	CH3	CH3	CH2OCH3	CH2O	2-Me-5-Cl-phenyl	Viscous liquid
122	CH3	CH3	propargyl	CH2O	2-Me-5-Cl-phenyl	Viscous liquid
123	CH3	CH3	CH2OCH3	CH2O	2-Me-5-SMe-phenyl	Viscous liquid
124	CH3	CH3	propargyl	CH2O	2-CHF2O-phenyl	Viscous liquid
125	CH3	CH3	CH2OCH3	CH2O	2-CHF2O-phenyl	Viscous liquid
126	CH3	CH3	propargyl	CH2O	3-CHF2O-phenyl	Viscous liquid
127	CH3	CH3	CH2OCH3	CH2O	3-CHF2O-phenyl	Viscous liquid
128	CH3	CH3	propargyl	CH2O	4-CHF2O-phenyl	Viscous liquid
129	CH3	CH3	CH2OCH3	CH2O	4-CHF2O-phenyl	Viscous liquid
130	CH3	CH3	propargyl	CH2O	2-Me-4-CHF2O-phenyl	Viscous liquid
131	CH3	CH3	CH2OCH3	CH2O	2-Me-5-CHF2O-phenyl	Viscous liquid
132	CH3	CH3	H	CH2O	2-Cl-4-CHF2O-phenyl	White crystal
133	CH3	CH3	CH2OCH3	CH2O	2-Cl-4-CHF2O-phenyl	Viscous liquid
134	CH3	CH3	propargyl	CH2O	2-Cl-4-CHF2O-phenyl	Viscous liquid
135	CH3	CH3	H	CH2O	2-Cl-5-CHF2O-phenyl	White crystal
136	CH3	CH3	CH2OCH3	CH2O	2-Cl-5-CHF2O-phenyl	Viscous liquid
137	CH3	CH3	propargyl	CH2O	2-Cl-5-CHF2O-phenyl	Viscous liquid
138	CH3	CH3	H	CH2O	5-Cl-2-CHF2O-phenyl	White crystal
139	CH3	CH3	CH2OCH3	CH2O	5-Cl-2-CHF2O-phenyl	Viscous liquid
140	CH3	CH3	propargyl	CH2O	5-Cl-2-CHF2O-phenyl	Viscous liquid
141	CH3	CH3	H	CH2O	2,5-(CHF2O)2-phenyl	White crystal
142	CH3	CH3	CH2OCH3	CH2O	2,5-(CHF2O)2-phenyl	Viscous liquid
143	CH3	CH3	propargyl	CH2O	2,5-(CHF2O)2-phenyl	Viscous liquid
144	CH3	CH3	propargyl	CH2O	2,4-(CHF2O)2-phenyl	Viscous liquid
145	CH3	CH3	H	CH2O	3-PhO-phenyl	White crystal

Table 1 (Continued)

146	CH3	CH3	CH2OCH3	CH2O	3-PhO-phenyl	Viscous liquid
147	CH3	CH3	propargyl	CH2O	3-PhO-phenyl	Viscous liquid
148	CH3	CH3	propargyl	CH2O	2-CF3-phenyl	Viscous liquid
149	CH3	CH3	CH2OCH3	CH2O	3-CF3-phenyl	Viscous liquid
150	CH3	CH3	propargyl	CH2O	4-CF3-phenyl	Viscous liquid
151	CH3	CH3	CH2OCH3	CH2O	2,5-(CF3)2-phenyl	Viscous liquid
152	CH3	CH3	propargyl	CH2O	2,5-(CF3)2-phenyl	Viscous liquid
153	CH3	CH3	CH2OCH3	CH2O	3,5-(CF3)2-phenyl	Viscous liquid
154	CH3	CH3	propargyl	CH2O	3,5-(CF3)2-phenyl	Viscous liquid
155	CH3	CH3	propargyl	CH2O	3-benzyloxy-phenyl	Viscous liquid
156	CH3	CH3	propargyl	CH2O	2-naphthyl	Viscous liquid
157	CH3	CH3	CH2OCH3	CH2O	2-naphthyl	Viscous liquid
158	CH3	CH3	propargyl	CH2O	3-naphthyl	Viscous liquid
159	CH3	CH3	CH2OCH3	CH2O	3-naphthyl	Viscous liquid
160	CH3	CH3	propargyl	CH2O	2,2-Me2-dihydrobenzofuran-5-yl	Viscous liquid
161	CH3	CH3	H	CH2ON=C(CH3)	phenyl	White crystal
162	CH3	CH3	CH2OCH3	CH2ON=C(CH3)	phenyl	Viscous liquid
163	CH3	CH3	propargyl	CH2ON=C(CH3)	phenyl	Viscous liquid
164	CH3	CH3	H	CH2ON=C(CH3)	3-CF3-phenyl	White crystal
165	CH3	CH3	CH2OCH3	CH2ON=C(CH3)	3-CF3-phenyl	Viscous liquid
166	CH3	CH3	propargyl	CH2ON=C(CH3)	3-CF3-phenyl	Viscous liquid
167	CH3	CH3	H	CH2ON=C(CH3)	4-CF3-phenyl	White crystal
168	CH3	CH3	CH2OCH3	CH2ON=C(CH3)	4-CF3-phenyl	Viscous liquid
169	CH3	CH3	propargyl	CH2ON=C(CH3)	4-CF3-phenyl	Viscous liquid
170	CH3	CH3	H	CH2ON=C(CH3)	3-Cl-phenyl	White crystal
171	CH3	CH3	propargyl	CH2ON=C(CH3)	3-Cl-phenyl	Viscous liquid
172	CH3	CH3	H	CH2ON=C(CH3)	4-Cl-phenyl	White crystal
173	CH3	CH3	propargyl	CH2ON=C(CH3)	4-Cl-phenyl	Viscous liquid
174	CH3	CH3	H	CH2ON=C(CH3)	3-CHF2O-phenyl	White crystal
175	CH3	CH3	propargyl	CH2ON=C(CH3)	3-CHF2O-phenyl	Viscous liquid

Table 1 (Continued)

176	CH3	CH3	H	CH2ON=C(CH3)	4-CHF2O-phenyl	White crystal
177	CH3	CH3	propargyl	CH2ON=C(CH3)	4-CHF2O-phenyl	Viscous liquid
178	CH3	CH3	H	CH2ON=C(CH3)	3-MeO-4-CHF2O-phenyl	White crystal
179	CH3	CH3	propargyl	CH2ON=C(CH3)	3-MeO-4-CHF2O-phenyl	Viscous liquid
180	CH3	CH3	H	CH2ON=C(CH3)	3-Me-4-CHF2O-phenyl	White crystal
181	CH3	CH3	propargyl	CH2ON=C(CH3)	3-Me-4-CHF2O-phenyl	Viscous liquid
182	CH3	CH3	H	CH2ON=C(CH3)	3-Cl-4-CHF2O-phenyl	White crystal
183	CH3	CH3	propargyl	CH2ON=C(CH3)	3-Cl-4-CHF2O-phenyl	Viscous liquid
184	CH3	CH3	propargyl	CH2ON=C(CH3)	2-naphthyl	Viscous liquid
185	CH3	CH3	propargyl	CH2ON=C(CH3)	3-CF3O-phenyl	Viscous liquid
186	CH3	CH3	propargyl	CH2ON=C(CH3)	4-CF3O-phenyl	Viscous liquid
187	CH3	CH3	propargyl	CH2ON=C(CH3)	3-MeS-phenyl	Viscous liquid
188	CH3	C2H5	propargyl	CH2ON=C(CH3)	3-CF3-phenyl	Viscous liquid
189	CH3	H	propargyl	CH2ON=C(CH3)	3-CF3-phenyl	Viscous liquid
190	C2H5	CH3	propargyl	CH2ON=C(CH3)	3-CF3-phenyl	Viscous liquid
191	CH3	CH3	H	CH=NOCH(CH3)	phenyl	White crystal
192	CH3	CH3	CH2OCH3	CH=NOCH(CH3)	phenyl	Viscous liquid
193	CH3	CH3	propargyl	CH=NOCH(CH3)	phenyl	Viscous liquid
194	CH3	CH3	H	CH=NOCH(CH3)	3-CF3-phenyl	White crystal
195	CH3	CH3	CH2OCH3	CH=NOCH(CH3)	3-CF3-phenyl	Viscous liquid
196	CH3	CH3	propargyl	CH=NOCH(CH3)	3-CF3-phenyl	Viscous liquid
197	CH3	CH3	H	CH=NOCH(CH3)	4-CF3-phenyl	White crystal
198	CH3	CH3	CH2OCH3	CH=NOCH(CH3)	4-CF3-phenyl	Viscous liquid
199	CH3	CH3	propargyl	CH=NOCH(CH3)	4-CF3-phenyl	Viscous liquid
200	CH3	CH3	H	CH=NOCH(CH3)	3-Cl-phenyl	White crystal
201	CH3	CH3	propargyl	CH=NOCH(CH3)	3-Cl-phenyl	Viscous liquid
202	CH3	CH3	H	CH=NOCH(CH3)	4-Cl-phenyl	White crystal
203	CH3	CH3	propargyl	CH=NOCH(CH3)	4-Cl-phenyl	Viscous liquid
204	CH3	CH3	H	CH=NOCH(CH3)	3-CHF2O-phenyl	White crystal
205	CH3	CH3	propargyl	CH=NOCH(CH3)	3-CHF2O-phenyl	Viscous liquid

Table 1 (Continued)

206	CH3	CH3	H	CH=NOCH(CH3)	4-CHF2O-phenyl	White crystal
207	CH3	CH3	propargyl	CH=NOCH(CH3)	4-CHF2O-phenyl	Viscous liquid
208	CH3	CH3	H	CH=NOCH(CH3)	3-MeO-4-CHF2O-phenyl	White crystal
209	CH3	CH3	propargyl	CH=NOCH(CH3)	3-MeO-4-CHF2O-phenyl	Viscous liquid
210	CH3	CH3	H	CH=NOCH(CH3)	3-Me-4-CHF2O-phenyl	White crystal
211	CH3	CH3	propargyl	CH=NOCH(CH3)	3-Me-4-CHF2O-phenyl	Viscous liquid
212	CH3	CH3	H	CH=NOCH(CH3)	3-Cl-4-CHF2O-phenyl	White crystal
213	CH3	CH3	propargyl	CH=NOCH(CH3)	3-Cl-4-CHF2O-phenyl	Viscous liquid
214	CH3	CH3	propargyl	CH=NOCH(CH3)	2-naphthyl	Viscous liquid
215	CH3	CH3	propargyl	CH=NOCH(CH3)	3-CF3O-phenyl	Viscous liquid
216	CH3	CH3	propargyl	CH=NOCH(CH3)	4-CF3O-phenyl	Viscous liquid
217	CH3	CH3	propargyl	CH=NOCH(CH3)	3-MeS-phenyl	Viscous liquid
218	CH3	CH3	propargyl	CH=NOCH2	3-CF3-phenyl	Viscous liquid
219	CH3	H	propargyl	CH=NOCH(CH3)	3-CF3-phenyl	Viscous liquid
220	CH3	C2H5	propargyl	CH=NOCH(CH3)	3-CF3-phenyl	Viscous liquid
221	CH3	CH3	H	CH2S	phenyl	White crystal
222	CH3	CH3	propargyl	CH2S	phenyl	Viscous liquid
223	CH3	CH3	H	CH2S	2,5-Cl2phenyl	White crystal
224	CH3	CH3	propargyl	CH2S	2,5-Cl2phenyl	Viscous liquid
225	CH3	CH3	H	CH2S	2-Cl-5-CHF2O-phenyl	White crystal
226	CH3	CH3	propargyl	CH2S	2-Cl-5-CHF2O-phenyl	Viscous liquid
227	CH3	CH3	propargyl	CH2S	4-CF3-pyridin-2-yl	Viscous liquid
228	CH3	CH3	H	CH2S	6-Cl-4-CF3-pyridin-2-yl	Viscous liquid
229	CH3	CH3	propargyl	CH2S	6-Cl-4-CF3-pyridin-2-yl	Viscous liquid
230	CH3	CH3	H	CH2S	benzothiazol-2-yl	White crystal
231	CH3	CH3	H	C≡C	3-CF3-Phenyl	White crystal
232	CH3	CH3	propargyl	C≡C	3-CF3-Phenyl	Viscous liquid
233	CH3	CH3	CH2OCH3	C≡C	3-CF3-Phenyl	Viscous liquid
234	CH3	CH3	propargyl	CH=CH	Phenyl	Viscous liquid
235	CH3	CH3	CH2OCH3	CH=CH	Phenyl	Viscous liquid

In Table 1, Me indicates a methyl group and Ph indicates a phenyl group.

The valu obtained in the analysis of the resulting compound by means of ^{1}H-NMR is as follows.

^{1}H-NMR data ($CDCl_3$) of the compound No. 21; 2.13 (3H, s), 3.59 (3H, s), 3.72 (3H, s), 4.95 (2H, s), 5.72 (1H, brs), 7.35 (5H, brs)

^{1}H-NMR data ($CDCl_3$) of the compound No. 22; 2.14 (3H, s), 3.6 (3H, s), 3.65 (3H, brs), 3.72 (3H, s), 4.4

(2H, brs), 4.95 (2H, s), 5.72 (1H, brs), 7.35 (5H, brs)

^{1}H-NMR data ($CDCl_3$) of the compound No. 23; 2.23 (3H, s), 2.24 (1H, dd), 3.62 (3H, s), 3.67 (3H, s), 3.93 (1H, dd), 4.63 (1H, dd), 4.85 (2H, s), 7.34 (5H, m)

^{1}H-NMR data ($CDCl_3$) of the compound No. 36; 2.19 (3H, s), 3.64 (3H, s), 3.76 (3H, s), 4.95 (2H, s), 6.07 (1H, brs), 7.22 (1H, dd), 7.33 (1H, d), 7.53 (1H, d)

^{1}H-NMR data ($CDCl_3$) of the compound No. 37; 1.85 (3H, t), 2.19 (3H, s), 3.64 (3H, s), 3.76 (3H, s), 4.7 (2H, br), 4.95 (2H, s), 7.22 (1H, dd), 7.33 (1H, d), 7.53 (1H, d)

^{1}H-NMR data ($CDCl_3$) of the compound No. 38; 2.2 (3H, s), 3.55 (3H, s), 3.6 (3H, brs), 3.70 (3H, s), 4.12 (1H, dd), 4.65 (1H, dd), 4.92 (2H, s), 7.23 (1H, d), 7.31 (1H, d), 7.50 (1H, s)

^{1}H-NMR data ($CDCl_3$) of the compound No. 40; 2.21 (3H, s), 2.27 (1H, dd), 3.64 (3H, s), 3.70 (3H, s), 4.12 (1H, dd), 4.65 (1H, dd), 4.92 (2H, s), 7.23 (1H, d), 7.31 (1H, d), 7.50 (1H, s)

^{1}H-NMR data ($CDCl_3$) of the compound No. 48; 2.18 (3H, s), 2.30 (3H, s), 2.34 (3H, s), 3.59 (3H, s), 3.72 (3H, s), 4.83 (2H, s), 6.55 (1H, brs), 7.0-7.2 (3H, m)

^{1}H-NMR data ($CDCl_3$) of the compound No. 50; 2.17 (3H, s), 2.24 (1H, dd), 2.31 (3H, s), 2.33 (3H, s), 3.64 (3H, s), 3.70 (3H, s), 3.89 (1H, d), 4.88 (1H, d), 4.79 (1H, d), 4.86 (1H, d), 7.08 (3H, m)

^{1}H-NMR data ($CDCl_3$) of the compound No. 65; 2.18 (3H, s), 3.63 (3H, s), 3.73 (3H, s), 4.97 (2H, s), 6.09 (1H, brs), 6.52 (1H, t), 7.05 (1H, dd), 7.30 (1H, d), 7.38 (1H, d)

^{1}H-NMR data ($CDCl_3$) of the compound No. 66; 2.19 (3H, s), 3.39 (3H, s), 3.61 (3H, s), 3.71 (3H, brs), 4.74 (1H, d), 4.93 (2H, s), 5.03 (1H, d), 6.52 (1H, t), 7.04 (1H, dd), 7.31 (1H, d), 7.36 (1H, d)

^{1}H-NMR data ($CDCl_3$) of the compound No. 67; 2.20 (3H, s), 2.26 (1H, t), 3.64 (3H, s), 3.69 (3H, brs), 4.08 (1H, dd), 4.62 (1H, dd), 4.88 (2H, s), 6.48 (1H, t), 7.09 (1H, dd), 7.32 (1H, d), 7.50 (1H, d)

^{1}H-NMR data ($CDCl_3$) of the compound No. 68; 2.17 (3H, s), 3.62 (3H, s), 3.74 (3H, s), 4.90 (2H, s), 6.09 (1H, brs), 6.46 (1H, t), 7.09 (1H, d), 7.31 (1H, dd), 7.50 (1H, d)

^{1}H-NMR data ($CDCl_3$) of the compound No. 69; 2.18 (3H, s), 3.39 (3H, s), 3.61 (3H, s), 3.73 (3H, brs), 4.70 (1H, d), 4.87 (2H, s), 5.03 (1H, d), 6.47 (1H, t), 7.09 (1H, d), 7.31 (1H, dd), 7.50 (1H, d)

^{1}H-NMR data ($CDCl_3$) of the compound No. 70; 2.19 (3H, s), 2.26 (1H, t), 3.63 (3H, s), 3.70 (3H, brs), 4.08 (1H, dd), 4.62 (1H, dd), 4.88 (2H, s), 6.48 (1H, t), 7.09 (1H, d), 7.32 (1H, dd), 7.50 (1H, d)

^{1}H-NMR data ($CDCl_3$) of the compound No. 71; 2.17 (3H, s), 3.62 (3H, s), 3.74 (3H, s), 4.90 (2H, s), 6.09 (1H, brs), 6.46 (1H, t), 6.53 (1H, t), 7.09 (1H, d), 7.31 (1H, dd), 7.50 (1H, d)

^{1}H-NMR data ($CDCl_3$) of the compound No. 72; 2.18 (3H, s), 3.39 (3H, s), 3.61 (3H, s), 3.73 (3H, brs), 4.70 (1H, d), 4.87 (2H, s), 5.03 (1H, d), 6.47 (1H, t), 6.56 (1H, t), 7.09 (1H, d), 7.31 (1H, dd), 7.50 (1H, d)

^{1}H-NMR data ($CDCl_3$) of the compound No. 73; 2.19 (3H, s), 2.26 (1H, t), 3.63 (3H, s), 3.70 (3H, brs), 4.08 (1H, dd), 4.62 (1H, dd), 4.88 (2H, s), 6.48 (1H, t), 6.56 (1H, t), 7.09 (1H, d), 7.32 (1H, dd), 7.50 (1H, d)

^{1}H-NMR data ($CDCl_3$) of the compound No. 75; 1.13 (3H, t), 2.08 (3H, s), 3.54 (3H, s), 3.60 (2H, br), 3.61 (3H, brs), 4.75 (1H, d), 4.82 (1H, d), 6.9-7.2 (6H, m), 7.3-7.4 (3H, m)

^{1}H-NMR data ($CDCl_3$) of the compound No. 76; 2.10 (3H, s), 3.37 (3H, s), 3.67 (3H, brs), 4.63 (1H, d), 4.80 (2H, s), 5.04 (1H, d), 6.95-7.16 (6H, m), 7.3-7.4 (3H, m)

^{1}H-NMR data ($CDCl_3$) of the compound No. 77; 2.11 (3H, s), 2.22 (1H, t), 3.62 (3H, s), 3.65 (3H, brs), 3.96 (1H, dd), 4.63 (1H, dd), 4.81 (2H, s), 6.92-7.18 (6H, m), 7.3-7.4 (3H, m)

^{1}H-NMR data ($CDCl_3$) of the compound No. 116; 2.14 (3H, s), 2.25 (3H, s), 2.26 (3H, s), 3.69 (3H, s), 3.75 (3H, s), 4.78 (2H, s), 6.25 (1H, brs), 6.80 (1H, d), 6.96 (2H, m)

^{1}H-NMR data ($CDCl_3$) of the compound No. 117; 2.13 (3H, s), 2.23 (1H, t), 2.26 (3H, s), 2.27 (3H, s), 3.68 (3H, brs), 3.71 (3H, s), 4.16 (1H, brd), 4.62 (1H, brd), 4.74 (2H, d), 6.78 (1H, d), 6.95 (1H, d), 6.96 (1H, s)

^{1}H-NMR data ($CDCl_3$) of the compound No. 164; 2.28 (3H, s), 2.33 (3H, s), 3.6 (3H, s), 3.7 (3H, s), 4.78 (2H, s), 6.2 (1H, brs), 7.2-7.8 (4H, m)

^{1}H-NMR data ($CDCl_3$) of the compound No. 165; 2.20 (3H, s), 2.32 (3H, s), 3.70 (6H, s), 3.75 (3H, brs), 4.22 (1H, dd), 4.75 (1H, dd), 4.94 (1H, d), 5.02 (1H, d), 7.48 (1H, t), 7.60 (1H, d), 7.79 (1H, d), 7.88 (1H, s)

^{1}H-NMR data ($CDCl_3$) of the compound No. 166; 2.20 (3H, s), 2.26 (1H, d), 2.32 (3H, s), 3.70 (6H, s), 4.22 (1H, dd), 4.75 (1H, dd), 4.94 (1H, d), 5.02 (1H, d), 7.48 (1H, t), 7.60 (1H, d), 7.79 (1H, d), 7.88 (1H, s)

^{1}H-NMR data ($CDCl_3$) of the compound No. 167; 2.21 (3H, s), 2.28 (3H, s), 3.69 (3H, s), 3.79 (3H, s), 4.95 (2H, s), 7.64 (2H, d), 7.71 (2H, d)

^{1}H-NMR data ($CDCl_3$) of the compound No. 169; 2.20 (3H, d), 2.27 (1H, t), 2.32 (3H, s), 3.70 (6H, brs), 4.23 (1H, dd), 4.77 (1H, dd), 4.94 (1H, d), 5.03 (1H, d), 7.61 (2H, d), 7.73 (2H, d)

^{1}H-NMR data ($CDCl_3$) of the compound No. 194; 1.58 (3H, d), 2.21 (3H, s), 3.69 (3H, s), 5.23 (1H, q), 7.08 (1H, brs), 7.4-7.6 (4H, m), 8.01 (1H, s)

^{1}H-NMR data ($CDCl_3$) of the compound No. 196; 1.58 (3H, d), 2.18 (1H, dd), 2.26 (3H, s), 3.68 (3H, s), 3.90 (1H, dd), 4.5 (1H, dd), 5.22 (1H, q), 7.4-7.6 (4H, m), 7.97 (1H, d)

^{1}H-NMR data ($CDCl_3$) of the compound No. 197; 1.57 (3H, d), 2.21 (3H, s), 3.68 (3H, s), 3.69 (3H, s), 5.25 (1H, q), 7.08 (1H, brs), 7.46 (2H, d), 7.61 (2H, d), 8.01 (1H, s)

^{1}H-NMR data ($CDCl_3$) of the compound No. 199; 1.56 (3H, d), 2.20 (1H, dd), 2.25 (3H, s), 3.68 (6H, brs), 4.52 (1H, dd), 5.22 (1H, q), 7.45 (2H, m), 7.6 (2H, m), 7.96 (1H, s)

^{1}H-NMR data ($CDCl_3$) of the compound No. 228; 2.27 (3H, s), 3.68 (3H, s), 3.83 (3H, s), 4.14 (2H, s), 5.5 (1H, brs), 7.77 (1H, d), 8.63 (1H, d)

^{1}H-NMR data ($CDCl_3$) of the compound No. 229; 2.35 (3H, s), 2.48 (1H, d), 3.94 (1H, d), 4.10 (3H, s), 4.12 (3H, s), 4.58 (1H, d), 4.94 (2H, s), 7.75 (1H, s), 8.62 (1H, s)

^{1}H-NMR data ($CDCl_3$) of the compound No. 230; 2.25 (3H, s), 3.67 (3H, s), 3.91 (3H, s), 4.24 (2H, s), 7.32 (1H, t), 7.47 (1H, t), 7.74 (1H, d), 8.02 (1H, d), 9.6 (1H, brs)

^{1}H-NMR data ($CDCl_3$) of the compound No. 231; 2.33 (3H, s), 3.73 (3H, s), 3.83 (3H, s), 6.35 (1H, brs), 7.46 (1H, t), 7.56 (1H, d), 7.63 (1H, d), 7.72 (1H, s)

^{1}H-NMR data ($CDCl_3$) of the compound No. 232; 2.27 (1H, t), 2.35 (3H, s), 3.71 (3H, s), 3.79 (3H, brs), 4.25 (1H, d), 4.85 (1H, d), 7.46 (1H, t), 7.56 (1H, d), 7.61 (1H, d), 7.70 (1H, s)

^{1}H-NMR data ($CDCl_3$) of the compound No. 233; 2.34 (3H, s), 3.46 (3H, s), 3.69 (3H, s), 3.80 (3H, brs), 4.89 (1H, d), 5.25 (1H, d), 7.45 (1H, t), 7.54 (1H, d), 7.60 (1H, d), 7.69 (1H, s)

Formulation Example 1

20 Parts of the compound No. 2 described in Table 1, 75 parts of diatomaceous earth and 5 parts of a surfactant containing alkylbenzenesulfonic acid as a main ingredient were uniformly pulverized and mixed to give a wettable powder.

Formulation Example 2

30 Parts of the compound No. 3 described in Table 1, 15 parts of "Sorpol" 3005X (trade mark of Toho Kagaku Co., Ltd., mixture of nonionic surfactant and anionic surfactant), 25 parts of xylene and 30 parts of dimethylformamide were sufficiently mixed to give an emulsifiable concentrate.

The following Test Examples illustrate that the compound of the present invention is useful as an agricultural/horticultural fungicide

Test Example 1 Preventive activity on wheat powdery mildow

Wettable powders prepared according to the same manner as that described in Formulation Example 1 were diluted with water to the predetermined concentration and then applied by foliar application on wheat plants (var. Norin No. 61) at the 1 to 2 leaf stage grown in pots of 6 cm in diameter at a ratio of 10 ml per one pot. After the chemical solution was air-dried, a spore suspension obtained from the leaf of wheat infected with Erysiphe graminis was spray-inoculated. After inoculation, the seedling of wheat was allowed to stand at room temperature for 7 to 10 days.

For evaluation, the diseased area ratio of each leaf was measured and the preventive value was calculated from the following equation:

$$\text{The preventive value (\%)} = \frac{\text{(average diseased area ratio in untreated plot)} - \text{(average diseased area ratio in treated plot)}}{\text{(average diseased area ratio in untreated plot)}} \times 100$$

The results are shown in the column under the item "preventive value 1" in Table 2.

The test compound No. cited in the Table 2 corresponds to the compound No. of Table 1.

Test Example 2 Preventive activity on wheat brown

Wettable powders prepared according to the same manner as that described in Formulation Example 1 were diluted with wat r to the predetermin d concentration and then applied by foliar application on wheat plants (var. Norin No. 61) at the 1 to 2 l af stage grown in pots of 6 cm in diamet r at a ratio of 10 ml per

one pot. After the chemical solution was air-dried, a spore suspension obtained by pulverizing the leaf of wheat infected with Puccinia recondita was spray-inoculated. After inoculation, the wheat seedling was maintained in a moist chamber at 22°C for 15 hours and was allowed to stand on a water tank in a green house for 7 days.

For evaluation, the diseased area ratio of each leaf was measured and the preventive value was calculated from the following equation:

$$\text{The preventive value (\%)} = \frac{\text{(average diseased area ratio in untreated plot)} - \text{(average diseased area ratio in treated plot)}}{\text{(average diseased area ratio in untreated plot)}} \times 100$$

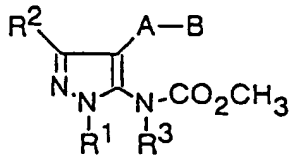
The results are shown in the column under the item "preventive value 2" in Table 2.

Table 2

Test compound No.	Concentration of active ingredient (ppm)	Preventive value 1 (%)	Preventive value 2 (%)
22	200	91	87
23	200	100	100
37	200	98	92
38	200	100	100
40	200	100	100
48	200	93	86
50	200	100	100
66	200	100	100
67	200	100	100
69	200	100	100
70	200	100	100
72	200	100	100
73	200	100	100
76	200	99	98
77	200	100	100
117	200	95	96
165	200	100	100
166	200	100	100
169	200	100	100
196	200	100	100
199	200	100	100
230	200	89	85
232	200	100	100

Claims

1. A N-pyrazolyl carbamate derivative represented by the general formula (I):



(I)

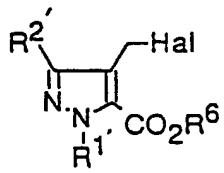
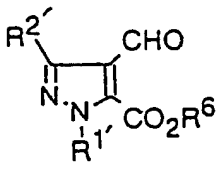
wherein R^1 and R^2 independently indicate a hydrogen atom or a C_1-C_4 alkyl group; R^3 is a hydrogen atom, a C_1-C_4 alkyl group, a C_2-C_5 alkynyl group, a C_2-C_4 alkylthioalkyl group or a C_2-C_4 alkoxyalkyl group; A is -O-, -C(O)-, $-OCH_2$-, $-CH_2O$-, $-CH_2S$-, -C≡C-, -CH=CH-, $-CH_2CH_2$-, $-CH_2ON=C(R^4)$- or $-CH=NOC(R^4)(R^5)$- (wherein R^4 and R^5 independently indicate a hydrogen atom or a C_1-C_4 alkyl group); and B is a hydrogen atom, an optionally substituted aryl group or an optionally substituted heterocyclic group.

2. The N-pyrazolyl carbamate derivative according to claim 1, wherein R^1 and R^2 indicate a C_1-C_4 alkyl group; R^3 is a hydrogen atom, a C_1-C_4 alkyl group, a C_2-C_5 alkynyl group or a C_2-C_4 alkoxyalkyl group; A is -O-, $-OCH_2$-, $-CH_2O$-, $-CH_2S$-, -C≡C-, -CH=CH-, $-CH_2ON=C(R^4)$- or $-CH=NOC(R^4)(R^5)$- (wherein R^4 and R^5 independently indicate a hydrogen atom or a C_1-C_4 alkyl group); and B is an aryl group or a heterocyclic group which may be substituted with a substituent(s) selected from a group consisting of a cyano group, a nitro group, a halogen atom, a C_1-C_4 alkylgroup, a C_1-C_4 haloalkyl group, a C_1-C_6 alkoxy group which may be substituted with a halogen atom or a C_3-C_6 cycloalkyl group, a C_1-C_6 alkylthio group, a C_2-C_6 alkenyloxy group which may be substituted with a halogen atom, a C_2-C_6 alkynyloxy group and a phenoxy, benzyloxy or pyridyloxy group which may be substituted by the cyano group, nitro group, halogen atom, C_1-C_4 alkyl group, C_1-C_4 haloalkyl group, C_1-C_6 alkoxy group which may be substituted with a halogen atom or a C_3-C_6 cycloalkyl group, C_1-C_6 alkylthio group, C_2-C_6 alkenyloxy group which may be substituted with a halogen atom or C_2-C_6 alkynyloxy group.

3. The N-pyrazolyl carbamate derivative according to claim 1, wherein R^1 and R^2 indicate a C_1-C_4 alkyl group; R^3 is a hydrogen atom, a C_1-C_4 alkyl group, a C_2-C_5 alkynyl group or a C_2-C_4 alkoxyalkyl group; A is -O-, $-OCH_2$-, $-CH_2O$-, $-CH_2S$-, -C≡C-, $-CH_2ON=C(R^4)$- or $-CH=NOC(R^4)(R^5)$-(wherein R^4 and R^5 independently indicate a hydrogen atom or a C_1-C_2 alkyl group); and B is an aryl group or a heterocyclic group which may contains a substituent(s) selected from a halogen atom, a C_1-C_4 alkyl group, a C_1-C_4 haloalkyl group, a C_1-C_6 alkoxy group which may be substituted with a halogen atom and a phenoxy group.

4. The N-pyrazolyl carbamate derivative according to claim 1, wherein R^1 and R^2 indicate a methyl group; R^3 is a hydrogen atom, a C_1-C_4 alkyl group, a C_2-C_5 alkynyl group or a C_2-C_4 alkoxyalkyl group; A is $-OCH_2$-, $-CH_2O$-, $-CH_2S$-, -C≡C-, $-CH_2ON=C(R^4)$- or $-CH=NOC(R^4)(R^5)$- (wherein R^4 is a hydrogen atom or a methyl group and R^5 is a hydrogen atom); and B is a phenyl group which may contains a substituent(s) selected from a group consisting of halogen atom, a C_1-C_4 alkyl group, a C_1-C_4 alkoxy group which may be substituted with a fluorine atom, a trifluoromethyl group and a phenoxy group.

5. A pyrazole-5-yl carboxylate derivative represented by the general formula:


(VIII) or

(XIII)

wherein $R^{1'}$ and $R^{2'}$ indicate a C_1-C_4 alkyl group; Hal is a chlorine atom or a bromine atom; and R^6 is a C_1-C_4 alkyl group as an intermediate for the production of the N-pyrazolyl carbamate derivative of claim 2 or 3.

6. The 1,3-dimethylpyrazole-5-yl carboxylate derivative according to claim 5, wherein $R^{1'}$ and $R^{2'}$ indicate a methyl group.

7. An agricultural/horticultural fungicide comprising the N-pyrazolyl carbamate derivative of claim 1 as an active ingredient.

8. An agricultural/horticultural fungicide comprising the N-pyrazolyl carbamate derivative of claim 2 as an active ingredient.

9. An agricultural/horticultural fungicide comprising the N-pyrazolyl carbamate derivative of claim 3 as an active ingredient.

10. An agricultural/horticultural fungicide comprising the N-pyrazolyl carbamate derivative of claim 4 as an active ingredient.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 94 11 9428

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP-A-0 571 326 (SANDOZ LTD ET AL.) * page 2 - page 3, line 24 *	1,7	C07D231/18 C07D231/38 A01N43/56
A	EP-A-0 483 851 (MITSUBISHI KASEI CORPORATION) * the whole document *	1,7	
A D	EP-A-0 433 899 (MITSUBISHI KASEI CORPORATION) * the whole document * & JP-A-4 217 668 (...)	1,7	
A,D	EP-A-0 129 830 (SDS BIOTECH K.K) * the whole document *	1,7	
A	PATENT ABSTRACTS OF JAPAN vol. 17, no. 644 (C-1134) (6273) 30 November 1993 & JP-A-05 201 980 (MITSUBISHI KASEI CORPORATION) 10 August 1993 * abstract *	1,7	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

C07D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	14 March 1995	Kyriakakou, G

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
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P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
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